Concentrated and dilutable solutions or dispersions, method of preparing same and uses thereof

The present invention relates to new concentrated and dilutable solutions or dispersions, their preparation process and to their uses.

A large number of liquid active agents can be used to effect in various fields but cannot be used as they are. In practice, because they will have too strong an effect if used neat, they have to be diluted, in the form of emulsions for an active liquid agent, for example. However, this then gives rise to a problem when it comes to recovery and reprocessing, particularly if they are harmful to the environment.

Conventionally, the dispersion of an organic solvent in an aqueous continuous phase in order to produce an emulsion requires the use of surfactants which are emulsifying in nature, hydrotropic agents such as xylene, toluene, or cumene sulphonate of sodium, and, more often than not, a third polar solvent such as isopropanol or glycol ethers. By way of illustration, a standard micro-emulsion of terpenic solvent will typically have the following composition: water / polyoxyethylenated fatty alcohols / polyoxyethylenated nonylphenols / sodium xylene sulphonate / isopropanol / terpenic solvent. Its life is limited, as is its temperature resistance. It can thus only be used cold.

Conventionally, micro-emulsions are obtained by progressively adding an aqueous phase to an organic phase (or vice versa) under constant agitation, in the presence of a surfactant and, if necessary, another solvent.

It would therefore be desirable to have the use of homogeneous compositions which are easy to produce, do not require thermal energy in the form of heating and can be readily recycled.

Micro-emulsions are homogeneous compositions but they contain significant concentrations of formulating agents, in particular emulsifiers and hydrotropic agents.

It would also seem desirable to be able to produce these stable micro-emulsions with the minimum of components other than water and the active agent to be emulsified.

WO-A-91/00893 describes paint and varnish strippers, optionally containing water, which are produced in the form of gels or bases with which organic clays such as bentones are impregnated. These compositions require the use of at least 10% of another water-soluble solvent of the N-methyl pyrrolidone type.

After lengthy research, the applicant has discovered, surprisingly, that new compositions, in the form of solutions or dispersions of a concentrated micro-emulsion type or a hydrophobic active agent or an N-alkyl pyrrolidone with water, satisfying the above criteria were able to be produced easily, using nothing more than a glycol ether or preferably a mixture of two glycol ethers.

Accordingly, the objective of the present application is to propose a composition in the form of a liquid/liquid dispersion of the micro-emulsion type or a solution of an active agent which is concentrated and dilutable in water, characterised in that it is transparent like water and essentially consists of

- at least 10 % by weight of a hydrophobic active agent having a KB (Kauri butanol) index higher than or equal to 30 and preferably 40 or less than 10% of an N-alkyl pyrrolidone and
- a glycol ether or preferably a mixture of two glycol ethers, the first glycol ether in the latter case having a HLB 0.8, preferably 0.9 and more particularly 1.0 higher than that of the second glycol ether.

In the present application and the description below, the term « essentially » is used to mean at least 90 % by weight of the composition, preferably at least 95 % and more particularly at least 98 %.

By « hydrophobic » is meant that the active agent has a low solubility in water. The water-solubility of the main active agent or agents will preferably be less than or equal to 8%, in particular less than or equal to 6%, more particularly less than or equal to 4%, most especially less than or equal to 1%.

If the composition is a micro-emulsion, it is for example water in oil (W/O), in particular « multiple » (O/W/O or W/O/W), and in particular oil in water (O/W).

The terms micro-emulsion used hereafter are therefore intended to mean solutions unless it is obvious from the context that only micro-emulsions could be meant.

If using a single glycol ether, it will have a high HLB. Dipropylene glycol methyl ether is more particularly used.

If two glycol ethers are used, dipropylene glycol methyl ether is used more specifically as the first glycol ether.

In order of decreasing HLB value as calculated by the Davies method, dipropylene glycol methyl ether (8.2), propylene glycol n-propyl ether (7.3), dipropylene glycol n-propyl ether (7.2), propylene glycol n-butyl ether (6.9) can for example be described.

The glycol ethers could for example represent 50 % to 90 % by weight of the concentrated micro-emulsion for example, in particular 60 % to 90 %, and more especially 70 % to 90 %.

If two glycol ethers are used, the ratio of the first glycol ether to the second glycol ether may range for example from 1:8 to 4:5, in particular from 1:5 to 3:5, and more especially from 1:3 to 2:5 by weight.

The active agent with a KB index which is preferably greater than or equal to 30 and in particular 40 will be chosen from among fatty substances, terpenic derivatives of synthetic, semi-synthetic or natural origin, rectified or not (by distillation) such as essential oils of pine, terpenes of citrus fruits, in particular orange such as d-limonene, non-water-soluble organic solvents of aliphatic petroleum origin such as the isoparaffins, certain carboxylated derivatives such as esters such as dimethyl esters, certain amides, carbonyl derivatives such as certain ketones, certain aldehydes, polar solvents other than terpenic alcohols, fatty alcohols (thus those having a high molecular weight), thiols, certain amines and ethers having for example 4 to 15 carbon atoms, preferably 5 to 14 carbon atoms, in particular 7 to 13 carbon atoms.

The active agent will preferably be selected from among the citrus terpenes, in particular orange; d-limonene is more especially preferred.

The active agent will more especially be d-limonene, an RPDE mixture of dimethyl esters or a mixture thereof.

They can also be active agents used in cosmetics, such as a hydrating agent like Evening Primrose oil, a soothing and scar-healing agent such as allantoin, an anti-UV agent such as phenoxyethanol or mexoryl®, an anti-ageing agent such as retinol, retinaldehyde, vitamin A acid, an exfoliating agent, an antioxidant or an active pharmaceutical agent which may be used in dermatology such as a corticosteroid.

The N-alkyl pyrrolidone is preferably N-methyl pyrrolidone.

It is obvious to a person skilled in the art that whenever this application talks of « a » given product, this is intended to mean « at least one » given product where justified by the context. This applies, for example, to the active agent, which may be a mixture of active agents, or to the emulsifiers.

The above micro-emulsions or solutions may also contain one or more conventional additives chosen for example from additives which are soluble in a non-aqueous phase such as perfumes and preservatives such as formol or the parabens. These can be used in the standard proportions generally used in micro- emulsions, in particular less than 5 %, especially 0.1 % to 3 %, and quite especially 0.1 % to 2 % by weight.

The additive might also be a preparation based on dimethylamides of unsaturated fatty acids such as that sold by BUCKMAN under the name of DMAD or BUSPERSE® 47.

The additives incorporated in the micro-emulsions or solutions described above impart specific properties to them such as biocidal properties. They may be rendered totally water-dilutable by adding surfactants of an emulsifying nature such as those sold by RHODIA under the name of Rhodoclean HP and/or ASP (alkoxylated fatty alcohols, derivatives of pine terpenes) and Rhodasurf T-50 (ethoxylated fatty alcohol) or by using an ether amine oxide.

The present application also relates to a concentrated micro-emulsion or solution as outlined above, characterised in that it is diluted so that the diluting phase, such as an isoparaffin solvent and in particular an aqueous phase, represents up to 99 % by weight of the diluted micro-emulsion or solution, in particular up to 80 %, preferably up to 60 %, more particularly up to 50 %, most particularly up to 40 %.

The present application also relates to a method of preparing a concentrated micro-emulsion or solution as outlined above, characterised in that the liquid active agent or active agents are mixed with the glycol ether or ethers under agitation in order to emulsify or dissolve them in the latter.

Although this preparation can be carried out hot, it has a remarkable advantage of being able to be carried out at ambient temperature and quickly, within a few minutes stirring, for example using a stirrer with 1 or 2 blades, that is to say the process requires a minimum of energy.

However, a non-liquid active agent should be melted or solubilized beforehand to convert it to liquid form.

The present application also relates to a method of preparing a diluted micro-emulsion, characterised in that the diluent and glycol ether or ethers are mixed with the liquid active agent or active agents to be emulsified under agitation. The mixing order is not critical. Under preferred conditions, a preliminary mixture of the diluent and glycol ether or ethers is prepared under agitation and the liquid active agent or active agents to be emulsified are then added progressively under continued agitation. By adding « progressively » is meant, for example, adding 10% V/V per minute.

The diluent is water or an aqueous phase in particular. It may also be an isoparaffin solvent in particular. It may also be a non-water-soluble aromatic organic solvent such as solvents of petroleum origin of the type such as white spirits.

A diluted micro-emulsion or solution may also be prepared by diluting a concentrated micro-emulsion or solution as outlined above.

This being the case, the glycol ether or ethers represent 15 % to 85% by weight of the diluted micro-emulsion, for example, in particular 20 % to 80 %, more particularly 25 % to 70 % and most especially 30 % to 50 %.

The aqueous phase, if used, is preferably constituted by water, in particular demineralised water. If it is not demineralised, the aqueous phase will preferably also contain a softening agent such as a phosphonate or the tetrasodium salt of ethylene diamine tetracetic acid. For a tap water of average hardness, for example, the softening agent may represent in the order of 0.5% by weight of the composition.

If desired, the aqueous phase may also contain one or more water-soluble compounds such as colorants.

To prepare standard micro-emulsions of solvents in water, it is necessary to adjust each of the constituents depending on the concentration of the solvents. It should be pointed out that one of the other remarkable qualities of the compositions according to the invention is that if two glycol ethers are used, the content of the second glycol ether merely has to be adjusted to enable the content of active agent(s) to be varied. Accordingly, it is possible to make micro-emulsions with different contents of active agent(s) without having to devise a specific formulation every time, i.e. without having to vary several parameters on the basis of the nature and quantity of the substances contained in the formulation.

The compositions proposed by the invention also exhibit a high degree of rinsability in water, in particular the active agents which do not exhibit this property by nature, and/or a capacity for aqueous dilution and phase separation in a manner that can be controlled and predetermined as desired.

The micro-emulsions or solutions proposed by the invention readily lend themselves to recycling. After use, the volume of non-aqueous effluents to be treated can be reduced by a simple aqueous dilution. The spent solution or micro-emulsion rapidly separates into two totally distinct phases, one of which is non-aqueous. As the phases separate, the glycol ethers are distributed within

each phase to facilitate the transfer and solubilization of the respective impurities and assist in producing a clearly defined interface.

The system proposed by the invention is totally reversible. The non-aqueous phase may be filtered and/or rectified with a view to recycling. Simply adding propylene glycol methyl ether and water will enable the initial product to be recreated.

This recycling process can be reinitiated at several points.

Using glycol ether(s) as proposed by the invention enables micro-emulsions of active agents to be obtained which are as different in chemical nature and polarity as d-limonene and mixtures of dimethyl esters, even if the same composition is used for the rest of the formula.

These properties are illustrated in the experimental part below.

The micro-emulsions proposed by the invention enable an excellent surface preparation to be made for mechanical parts prior to assembly or can be applied as a protective coating. They may be used on most metals, alloys, plastics materials and elastomers, particularly for the purpose of external maintenance on aircraft.

They enable compositions to be prepared which are excellent in terms of chemical innocuousness for use on joints and sensitive materials (polycarbonates, EPDM). After use, a surface will be non-greasy with no impurity or residual film.

It is also possible to regulate the rate at which the solvents used as active agents evaporate and they generally conserve a flash point higher than 61° C; this increases with the content of diluent phase, particularly water. Accordingly, the performance obtained is equal to that obtained with the halogenated solvents known from the prior art but without their harmful effects on the environment.

These properties warrant the use of the micro-emulsions or solutions proposed by the invention as an industrial solvent, a cleaner-renovator or as a surface treatment for plastic materials such as garden furniture, a cleaner-renovator for stained or darkened wood and as a cleaner for polyurethane foams.

They also justify use of the micro-emulsions or solutions proposed by the invention as a means of removing residues of mastic, cleaning paint brushes, removing glues and adhesives and diluting all types of paint. They also find applications in the nautical field (washing woods, plastic materials, mechanical elements, ...) especially as they can be rinsed with seawater unlike detergents, or alternatively for stripping in the case of those containing a N-alkyl pyrrolidone. They can likewise be used to maintain and renovate painted facades, roofing, boarding, aluminium and wooden joinery, for removing certain types of graffiti from buildings, cleaning pedestrian walkways, market places, public places, lorries and household refuse containers, fixtures and furnishings on the public highways, washing the exterior of vehicles and boats, cleaning textiles such as dusters, work clothes, in particular operative sites, blinds, floor coverings, carpets and rugs, removing the varnish from and defluxing electronic printed circuit boards. They also find applications in printing, in particular for cleaning screens, particularly made from silk.

The invention therefore also relates to washing or stripping agents containing a diluted micro-emulsion as proposed by the invention or a concentrated micro-emulsion or solution as defined above.

The preferred conditions of use described in relation to the solutions, micro-emulsions and concentrates described above also apply to the other aspects of the invention mentioned above.

The examples set out below illustrate the present application.

EXAMPLES 1 to 3

Diluted micro-emulsions were prepared using the following formula:

	Content by % Weight/ Weight		
	Ex. 1	**Ex. 2**	**Ex 3**
Demineralised water	to make up 100 %	to make up 100 %	to make up 100 %
Dipropylene glycol methyl ether	25.0 %	80.0 %	85.0 %
Propylene glycol n-butyl ether	0	0	0
D-limonene	0	2 to 10 %	10 %
RPDE mixture of dimethyl esters *	2 to 10 %	0	0

* Mixture of dimethyl esters sold by the RHODIA Company under the name of RPDE (dimethyl glutarate, succinate and adipate).

The micro-emulsions listed above were prepared as follows:

Whilst applying constant agitation, dipropylene glycol methyl ether is incorporated very progressively in demineralised water over a period of 5 minutes until the mixture is transparent. Still under constant agitation, the RPDE mixture of dimethyl esters or d-limonene is incorporated. Agitation is continued for a further 5 minutes, checking to ensure that the micro-emulsion is homogeneous, by observing its transparency for example.

It may be observed that using 25 % by weight of the single dipropylene glycol methyl ether will enable from 2 to 10 % of the RPDE dimethyl ester mixture to be emulsified. Using this single ether in a proportion of 80 % will emulsify from 2 to 10 % of d-limonene. The amount of water is the quantity needed to make up 100 % by weight in both cases.

<u>EXAMPLES 4 to 6</u>

Diluted micro-emulsions were prepared using the following formula:

	Content by % W ight/ Weight		
	Ex. 4	Ex. 5	Ex 6
Demineralised water	to make up 100 %	to make up 100 %	to make up 100 %
Dipropylene glycol methyl ether	27.0 %	26.0 %	45.0 %
Propylene glycol n-butyl ether	10.0 %	5 to 15 %	25.0 %
D-limonene	0	0	10 %
Mixture of dimethyl esters RPDE	2 to 20 %	15.0 %	0

These micro-emulsions were prepared as follows:

Whilst applying constant agitation, the dipropylene glycol methyl ether and the propylene glycol n-butyl ether are incorporated very progressively in demineralised water for a period of 5 minutes. Still applying constant agitation, the RPDE mixture of dimethyl esters or d-limonene is incorporated. Agitation is continued for a further 5 minutes and a check is made to ensure that the micro-emulsion is homogeneous, by observing its transparency for example.

It may be observed that a composition containing 27 % dipropylene glycol methyl ether and 10 % of propylene glycol n-butyl ether will enable from 2 % to 20 % of the RPDE dimethyl ester mixture to be emulsified without having to make any adjustment to the formula other than the amount of water needed to make up a quantity of 100 % by weight.

It may also be observed that a stable micro-emulsion is obtained, containing 15 % of RPDE dimethyl ester mixture using a mixture of 26 % of dipropylene glycol methyl ether with from 5 to 15 % of propylene glycol n-butyl ether. Here too, water is added to make up the quantity to 100 % by weight.

It may also be noted (see examples 3 and 6) that a stable micro-emulsion as proposed by the invention can be prepared from 10 % of d-limonene containing 5 to 20 % of water if using 85 % of dipropylene glycol methyl ether in the first instance and 45 % of this glycol plus 25 % of propylene glycol n-butyl ether in the second instance.

EXAMPLES 7 and 8

Concentrates were prepared for a micro-emulsion using the following formula:

	Content by % Weight/ Weight	
	Ex. 7	**Ex. 8**
Dipropylene glycol methyl ether	48.0 %	62.0 %
Propylene glycol n-butyl ether	22.0 %	20.0 %
RPDE mixture of dimethyl esters	30.0 %	18.0 %

These micro-emulsions were prepared by mixing the dipropylene glycol methyl ether and propylene glycol n-butyl ether for 5 minutes until the mixture is clear, followed by the RPDE mixture of dimethyl esters whilst continuing the constant agitation. Agitation is continued for a further 5 minutes and a check is made to ensure that the micro-emulsion is homogeneous.

After Example 7 is diluted 1/1 with water, the diluted micro-emulsion of Example 5 can be obtained if desired, containing 11.0 % of propylene glycol n-butyl ether.

The micro-emulsion of Example 8 can be diluted in any proportion, particularly in water.

EXAMPLES 9 to 12

Diluted micro-emulsions were prepared as specified in examples 1 to 3 in compliance with the following formula:

	Content by % Weight/ Weight			
	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Demineralised water	53.0 %	10.0 %	49.0 %	20.0 %
Dipropylene glycol methyl ether	27.0 %	80.0 %	26.0 %	45.0 %
Propylene glycol n-butyl ether	10.0 %	-	10.0 %	25.0 %
D-limonene	-	10.0 %	-	10.0 %
RPDE mixture of dimethyl esters	10.0 %	-	15.0 %	-
Water	34.0 %	6.0 %	12.0 %	10.0 %

The last row of the table represents the quantity of aqueous phase, for example water, from which the organic phase is made to salt out and the micro-emulsions assume a capacity to absorb water for example, i.e. can be diluted.

EXAMPLE 13: Salting out test

Having then used, for example, 100 g of the original micro-emulsion obtained in Example 6 (representing 100% by weight) to degrease mechanical car components, 40 ml of water were added to the original soiled micro-emulsion, which was shaken and then left to settle, as a result of which a cloudy appearance was observed, which was evidence that the composition was losing its homogeneity, after which a splitting of phases was observed whereby two clear phases were formed one on top of the other with a very marked separation on a level with the interface. The hydrophilic phase represents 92 ml for 65.3 ml at the outset. Since 40 ml of water were added, approximately 80% of the initial hydrophilic phase was therefore recovered.

Due to the properties of the compositions proposed by the invention, only a reduced volume of liquid has to be treated.

Furthermore, a very large proportion of organic top phase (propylene glycol n-butyl ether and d-limonene) can also be recovered and used to prepare a fresh initial micro-emulsion.

From an initial micro-emulsion comprising water (40 %), dipropylene glycol methyl ether (24 %), propylene glycol n-butyl ether (15 %), RPDE mixture of dimethyl esters (21 %), approximately 95.5 % of the initial hydrophilic phase was recovered by adding 40 ml of water.

EXAMPLES 14 to 18

Diluted micro-emulsions were prepared as specified in examples 1 to 3 based on the following formula:

	Content by % Weight/ Weight				
	Ex. 14	Ex. 15	Ex. 16	Ex. 17	Ex. 18
Demineralised water	20.0 %	25.0 %	62.5 %	20 %	67.5 %
Dipropylene glycol methyl ether	45.0 %	37.5 %	20.0 %	40.0 %	15.0 %
Propylene glycol n-propyl ether	25.0 %	27.5 %	-	-	7.5 %
Dipropylene glycol n-propyl ether	-	-	7.5 %	30 %	-
D-limonene	*	10.0 %	-	10.0 %	-
RPDE mixture of dimethyl esters	*	-	10.0 %	-	10.0 %

* Ex. 14: 10 % of RPDE mixture of dimethyl esters or d-limonene

This Example 14 demonstrates that by using glycol ether(s) as proposed by the invention, a micro-emulsion of active agents can be obtained which are as varied in terms of chemical nature and polarity as d-limonene and the dimethyl ester mixtures.

EXAMPLE 19

A micro-emulsion was prepared in accordance with the formula given for Example 18 but the RPDE mixture of dimethyl esters was replaced by a 5% mixture of said RPDE mixture of dimethyl esters and 5 % of d-limonene.